# Ultrafast Photochemistry of the $S_2$ State of Acetone and Dynamics of the Acetyl Radical

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# ABSTRACT

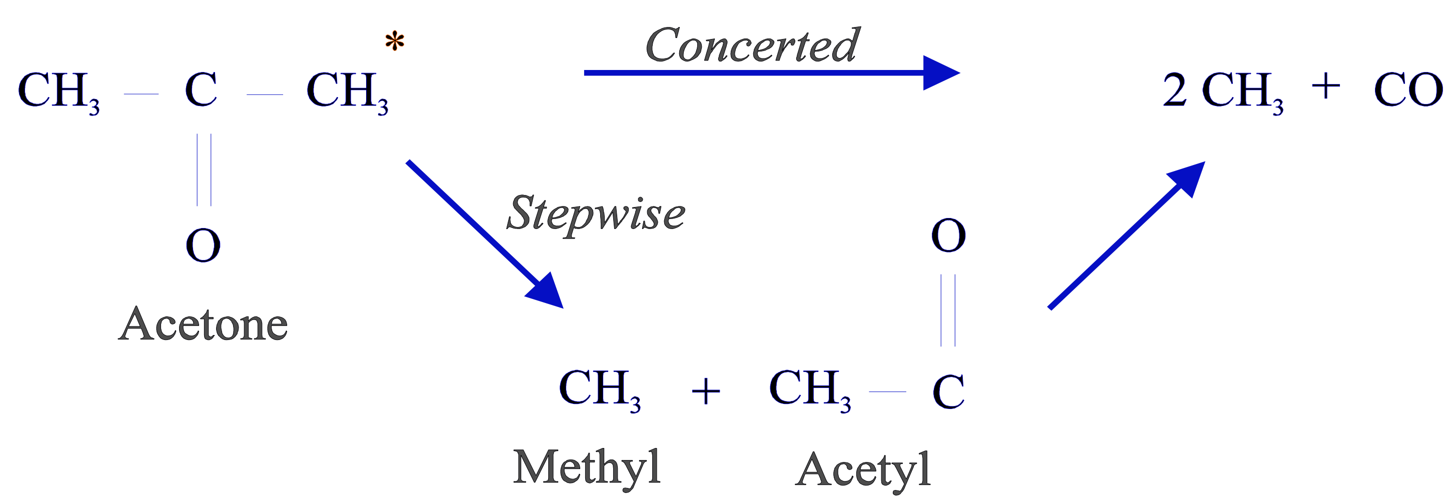
The photodissociation dynamics of the $S_2$, 3s Rydberg state of acetone (the $\tilde{B}$ state) and of the acetyl intermediate have been investigated using deep UV, mass-resolved, ultrafast photoionization spectroscopy. The experiments employ single photon excitation at 193–195 nm with probe pulses near 260 nm (for 1+1) and 390 nm (for 2+2). In either case, from the photoionization signal at the parent ion mass, the Rydberg state lifetime is determined to be 4.7ñ0.2 ps. Signals due to probe-induced ionization of the neutral acetyl intermediate were obtained using two photon ionization at 386 nm, which decreases the internal energy required for ionization compared to single photon detection at 260 nm. The acetyl lifetime was measured to be 3.1ñ0.5 ps. These results demonstrate that acetone dissociates sequentially for excitation to the $S_2$ state. The primary dissociation is relatively slow and the subsequent acetyl intermediate dissociates more rapidly. The measured lifetimes indicate that considering a description of the dissociation dynamics by an entirely statistical model is warranted. Our measurements illustrate that the photodissociation dynamics are different for excitation to various electronic states of acetone.

# Photochemistry of Acetone

Acetone

- Multiple dissociation of two equivalent bonds
- Smallest and prototypical ketone
- Testing ground for accurate description and suitable models for photodissociaton
    - Stepwise or concerted? Prompt or slow? Impulsive or Statistical?
    - Absolute and relative dissociatoin rates: distinguishing factors
    - Are all electronic states created equal?

        $S_2$ Rydberg (195 nm), $\{S_1 T_1\}$ valence (260 nm) , 4s Rydberg (150 nm)

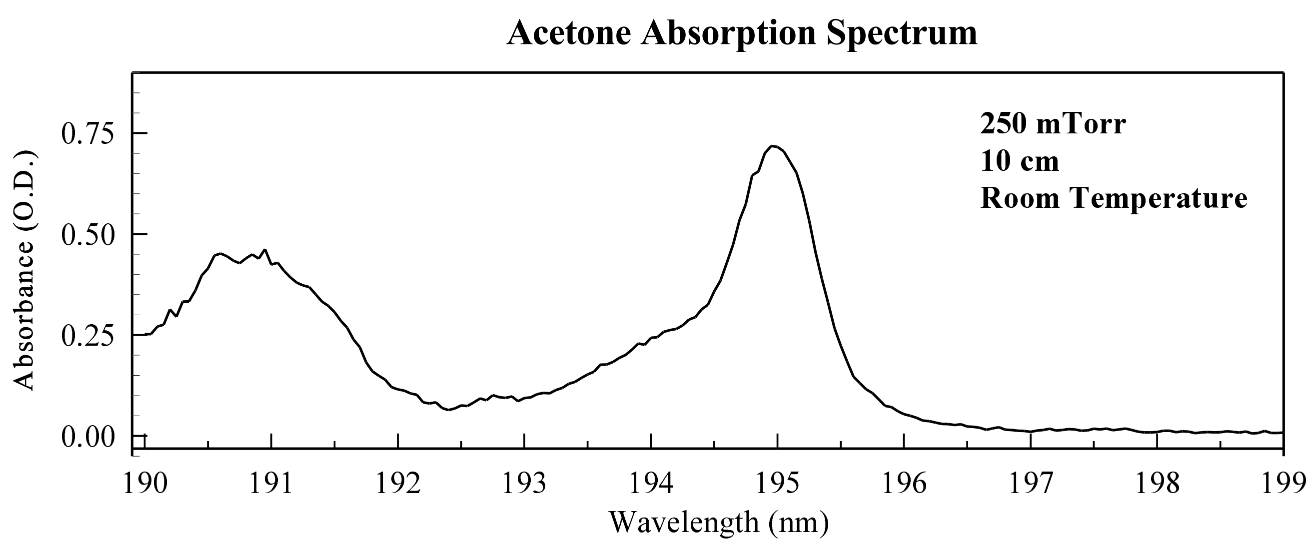


# Acetone $S_2$ Photochemistry: Background & Previous Studies

<u>Spectroscopy of $S_2$ State</u>

- 3s Rydberg or $\tilde{B}$ state:  promotion of oxygen electron: nþ3s
- Absorption bands
  - resolved vibronic structure but rotationally/torsionally diffuse þ predissociation
  - strong transition, $\text{þ}_0$ = 195.3 nm

    another þbandþ 190–193 nm: vibrations in CCC bend, $CH_3$ rock and deform.
  - 17 $cm^{-1}$ linewidths from jet-cooled spectra[1]þ lifetime ò300 fs
  - acetyl intermediate indicated by MPI power dependence[2]



# Product Translational and Internal Energy-Resolved Studies

- Near unity quantum yield[3] for dissociation to $2CH_3 + CO$:
  acetyl not directly detected
- Stepwise mechanism suggested:
  - high rotational temperatures in products[4]
  - two $CH_3$ translational energy distributions from analysis (& isotropic products)[5]
- More methyl internal energy measured recently[6] than previously[7]
  - interpretation of mechanism evolved from concerted to stepwise
  - neither fully impulsive or statistical models account for energy distributions

- 17ñ1 kcal barrier to acetyl dissociation[8]
- Dynamics for $S_2$ widely described as similar to $S_1$
  - $S_1$ is purely dissociative valence state, $\tilde{A}-\tilde{X}$ band is broad & near 260 nm
  - for $S_1$, stepwise mechanism demonstrated
    acetyl intermediates observed and $CH_3$ trans. energy peaks resolved[5]

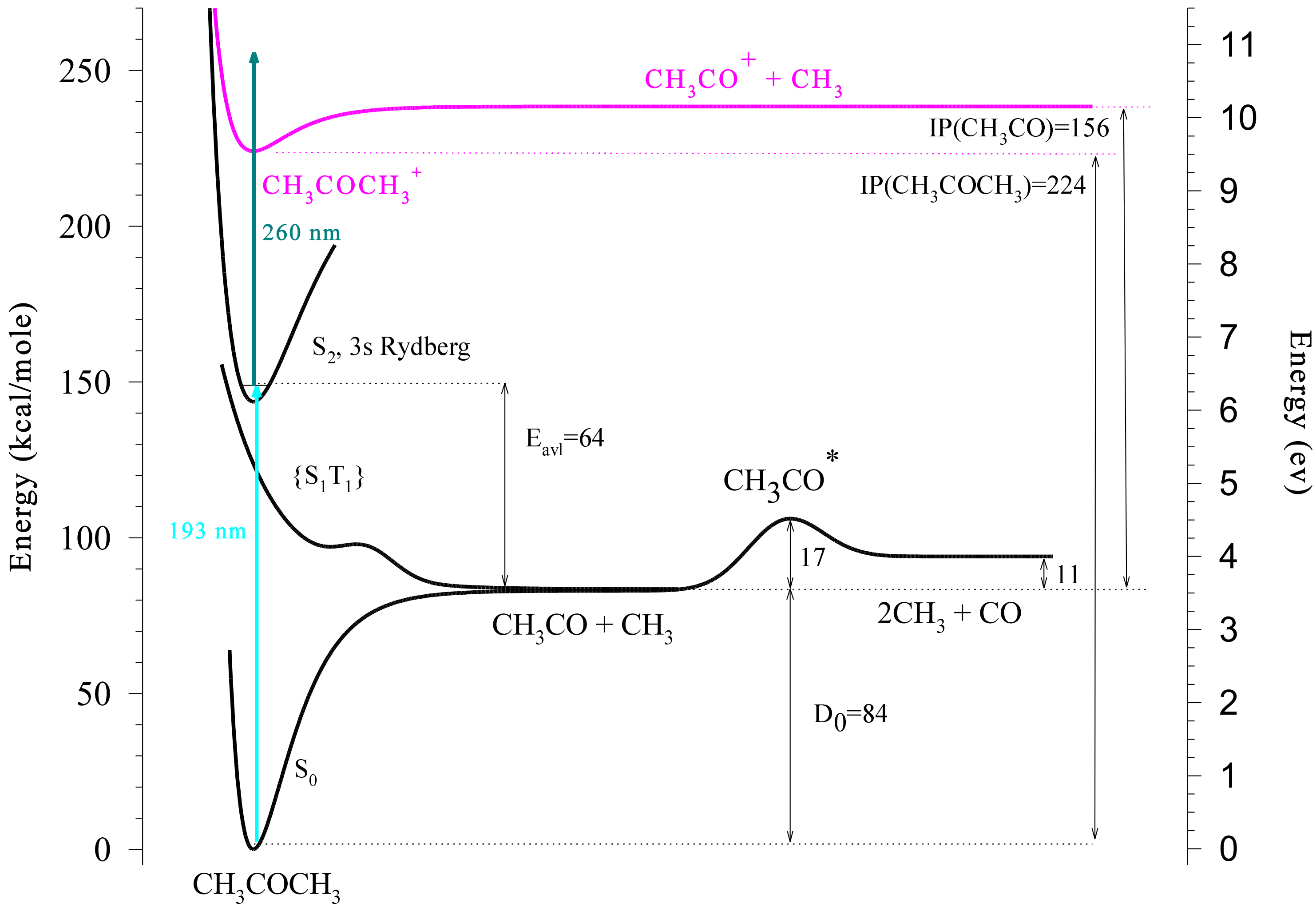
# Mass-Resolved Ultrafast Studies

- Kim et al.[9]: 2 photon excitation with 307 and 280 nm to near 4s state (also $d_6$)
  - stepwise, fast acetone dissociation (50 fs) – prompt
  - acetyl diss. time longer: 500 fs for excitation at 2þ307nm, 180 fs for 2þ280 nm
    dissociation rates are RRKM-like assuming impulsive energy partitioning
  - also investigated other acetyl precursors: (MEK, DEK, acetyl chloride)[10]
    inferred acetyl internal energy from dissociation rate using RRKM calc.:
    assessed limiting models: relative rates þ statistical; absolute þ impulsive

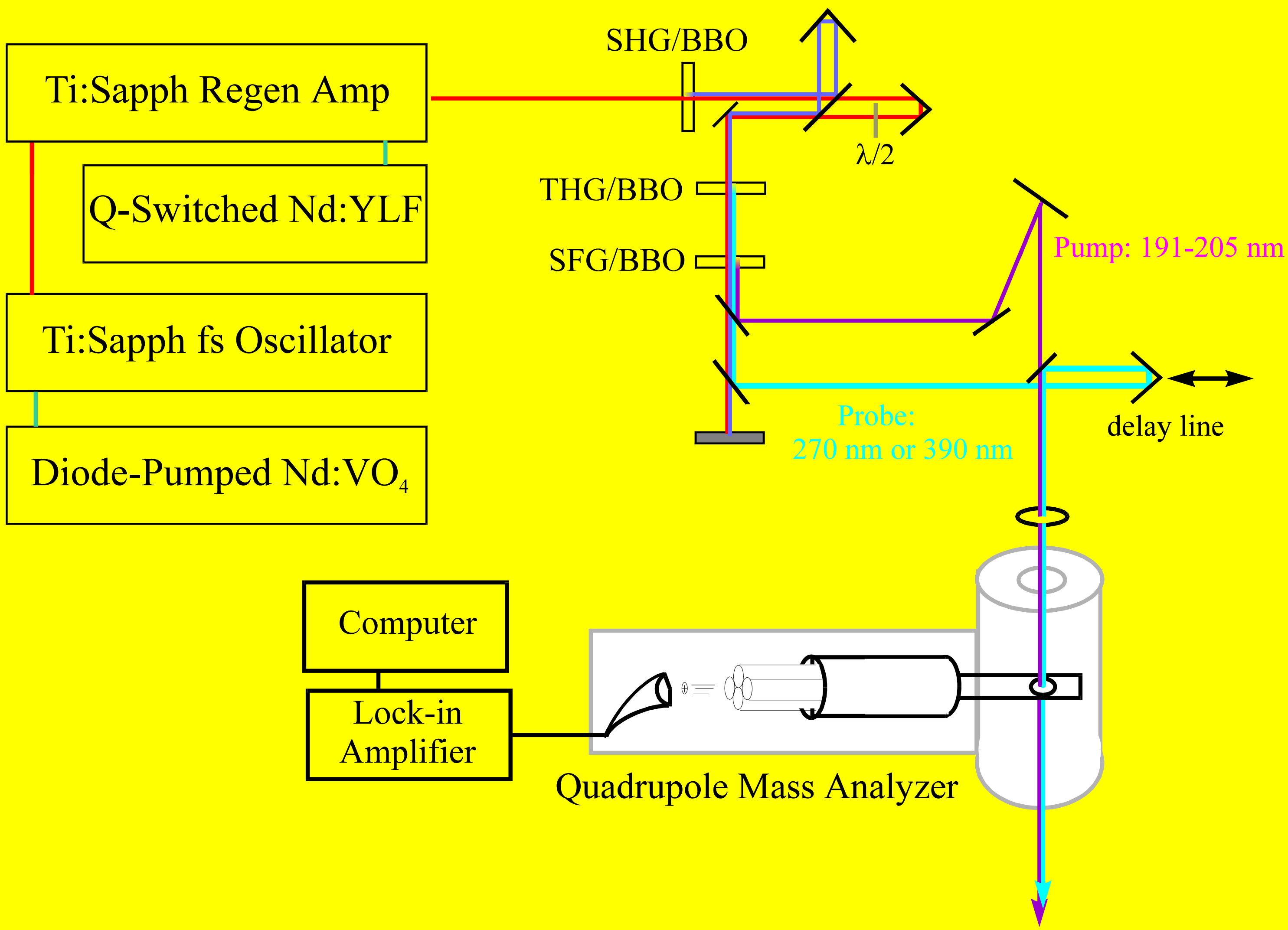
- Buzza et al.[11]: 3+2 MPI with 585 nm to $S_2$
  - acetone – not observed at parent ion, instrument-limited from acetyl
  - 1.7 ps dissociation time for acetyl monomer close to their RRKM calculation
  - interpretation inconsistent with energetics
    minimum internal energy too high for probe energy

# Potential Energy Surfaces for Acetone Photodissociation

adapted from Trentelman et al.[7]



# Femtosecond, Mass-Resolved Deep UV MPI



# Experimental Approach

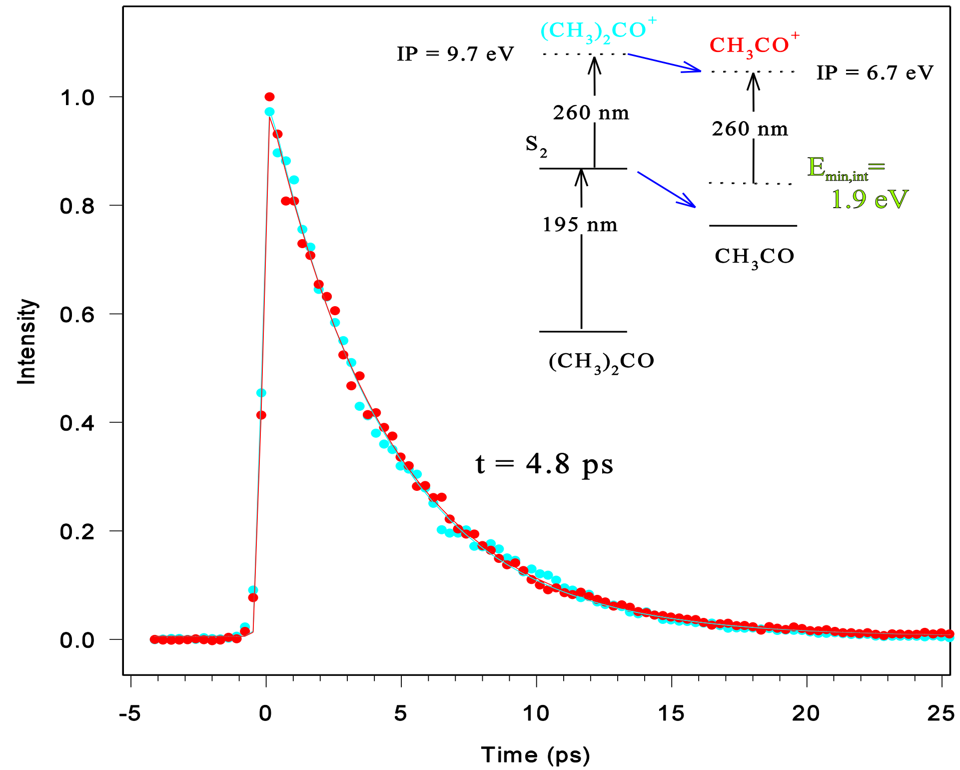
## Mass–Resolved Femtosecond Photoionization Spectroscopy

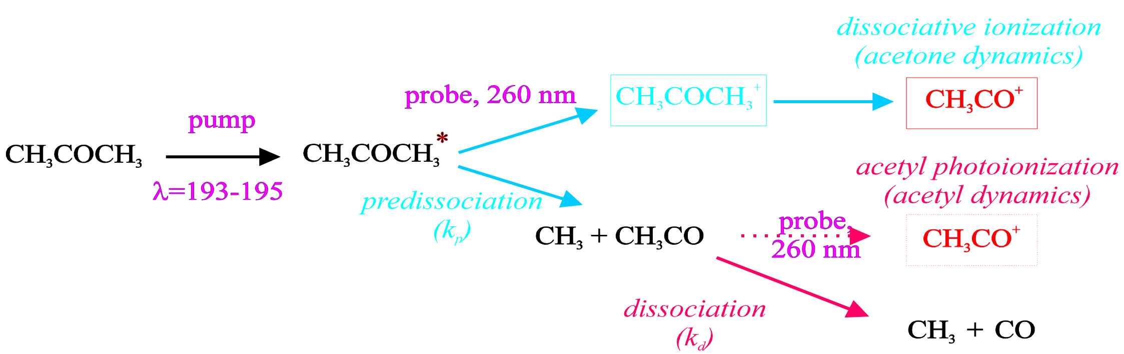
| Excitation | Probe | Detection |
|---|---|---|
| Single photon<br>Deep UV femtosecond<br>(193–195 nm; þ1 æJ)<br>þ<br>Sum frequency generation<br>btwn 3$^{rd}$ harm. and fund.<br>(BBO+long þþfs short þ) | Single photon<br>(260 nm; þ6 æJ) or<br>Two photon<br>(396 nm; þ50 æJ)<br>þ<br>3$^{rd}$ and 2$^{nd}$<br>harmonics | Mass–resolved<br>photoion detection<br>þ<br>Quadrupole mass spectrometer<br>and flowing sample at 2–<br>6x10$^{-5}$ Torr |

þ þ

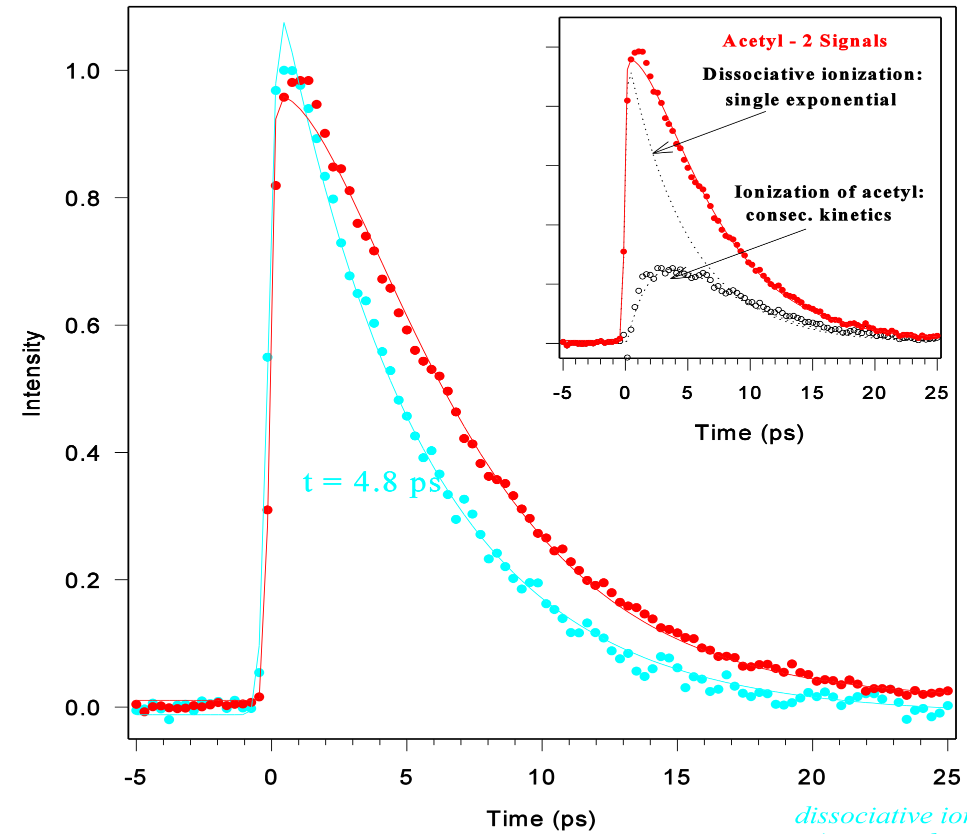
Regeneratively Amplified Ti:Sapphire Laser System

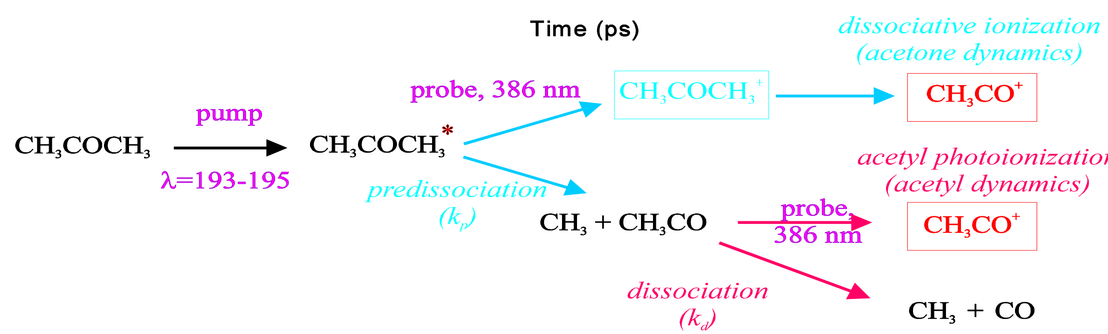
**Acetone and Acetyl**
**195 + 260 nm**




**Acetone and Acetyl**
**195 + 386 nm**
$E_{min,int}$ = 0.34 eV



# Results and Interpretation

Acetone: 193–195 + [260 (1+1) or 386 (1+2)] $S_2$ lifetime = 4.7 ñ 0.3 ps

Acetyl 193 + 260 (1+1) $E_{min}$=1.93 eV dissociative ionization

$E_{avl}$=2.8 eV 193 + 386 (1+2) $E_{min}$=0.34 eV not single exponential

Response function for signal at acetyl ion mass:

Consecutive dissociation kinetics

Dissociative ionization

$$S(t) \propto f_{cons} \left( \frac{e^{-k_p t} - e^{-k_d t}}{k_d - k_p} \right) + (1 - f_{cons})\, e^{-k_p t}$$

Acetyl dissociation time at 193 nm

kinetics of signal at 386 nm

$c_d$ = 1/$k_d$ = 3.1 ñ 0.5 ps

$f_{cons}$=0.15

Consec. fraction

# Discussion

$S_2$ Rydberg State Photodissociation Dynamics

- Sequential dissociation mechanism, primary and secondary steps resolved
- Acetone $S_2$ state is long-lived – not prompt or impulsive
  - straightforward explanation for isotropic products
  - consistent with limits from absorption linewidths
  - time for vibrational energy redistrib. – reconsider fully statistical mechanism

- Acetyl dissociation – faster than acetone
  - RRKM calculation[12] for acetyl: 3.1ñ0.5 ps þ $E_{int}$ = 25 ñ0.6 kcal/mole
    assuming typical $P(E_{int})$: consistent w/ no undissociated acetyl
  - $E_{int}$ not well established from other work:
    193 photofrag. trans. energy studies:<45 kcal/mol (2 eV)[5]

**Single photon 193 excitation:**
**Acetone dissociates from the $S_2$ state Slowly and Stepwise**

# Dissociation from $S_2$ vs. Other Electronic States of Acetone

. We have also studied acetone using 270 nm excitation – different than $S_2$
  - One photon excitation to $S_1$:
    - þ stepwise mechanism well established from product studies
    - þ acetone dissociation instrument–limited, prompt (<200 fs), impulsive?
    - þ acetyl partial dissociation (þ30%) with very long (>100 ps) lifetime
    - þ consistent with product studies
  - Two photon excitation to/near 4s Rydberg
    - þ results similar to Kim et al.[9]
    - þ acetone dissociation instrument limited, prompt (<200 fs)
    - þ acetyl dissociation rate close to RRKM calc. w/ impulsive energy partitioning

. $S_2$ state lifetime longer than for both $S_1$ and 4s Rydberg states – different mechanisms

. Acetyl dissociation rate increases with available energy

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